

L186.504



PATENT SPECIFICATION

NO DRAWINGS

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Inventors: LESLIE THOMAS ALLAN, GEOFFREY TATTERSALL NEWBOLD and ALBERT PERCIVAL

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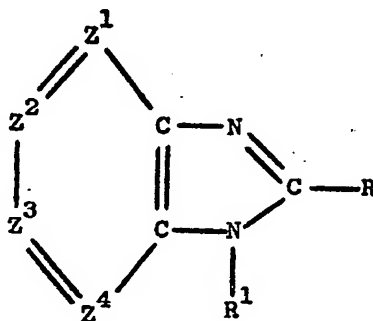
COMPLETE SPECIFICATION

Substituted Heterocyclic Compounds

We, Fisons Pest Control Limited, a British Company, of Harston, Cambridgeshire, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

5 The present invention relates to certain substituted imidazopyridines which have been found to possess biocidal activity, to their preparation and to agricultural and other compositions containing the same. The substituted imidazopyridines as herein-
after described are active in many fields and these compounds are exceptionally active as herbicides.

10 Accordingly the present invention is for the substituted imidazopyridines of the general formula:—



15 where R is a straight chain or branch chain alkyl (for example methyl, ethyl, isopropyl, tertiary butyl or amyl), alkenyl (for example vinyl or allyl), or alkynyl (for example ethynyl) group or an aryl (for example phenyl), aralkyl (for example benzyl) or cyclo-
alkyl (for example cyclopentyl or cyclohexyl) group, all of which groups may be un-
substituted or substituted, for example by the groups alkyl, halogen and nitro (e.g. nitrophenyl, chlorobenzyl, methylcyclopropyl) and where R¹ is hydrogen, alkyl for ex-
ample of 1—4 carbon atoms such as methyl or ethyl, substituted alkyl (for example beta-
20 ethoxyethyl or alkyl substituted by a further imidazopyridine group, aralkyl (for
example benzyl), substituted aralkyl (for example chlorobenzyl), aryl or substituted
aryl (for example chlorophenyl), —CY¹Y²R² or —COR², where Y¹ and Y² are oxygen
or sulphur, and where R² is alkyl (for example of 1—6 carbon atoms such as methyl,
ethyl or propyl), substituted alkyl (for example chloromethyl or bromoethyl), aryl (for
25 example phenyl or naphthyl) or substituted aryl (for example tolyl or xylyl), —SR³,
where R³ is polyhalogenated alkyl (such as trichloromethylthio); and where one of
Z¹, Z², Z³ and Z⁴ is a nitrogen atom and the remaining groups are CR², CR² and

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CR¹, where R², R³ and R⁴ are the same or different and are selected from the group consisting of hydrogen, alkyl (for example 1—6 carbon atoms such as methyl, ethyl or propyl), hydroxy, alkoxy (for example methoxy, ethoxy or butoxy), substituted alkoxy, aryloxy (for example phenoxy) or substituted aryloxy (for example chlorophenoxy), nitro, halogen (for example chloro, bromo or fluoro), pseudo-halogen (i.e. cyano, thiocyno, isothiocyno or azido), substituted alkyl (for example trifluoromethyl, chloromethyl, bromomethyl, trichloromethyl, hydroxymethyl, 2-chloroethyl, 2-hydroxyethyl or 2-methoxyethyl), carboxy, carboxy ester, carboxy amide, N-mono-substituted or di-substituted carboxy amide, amino or mono- or disubstituted amino (for example methylamino, dimethylamino, acetylamino, trifluoroacetylamino, benzenesulphonamido, paratoluenesulphonamido, methanesulphonamido), thiol, alkylthiol, and oxygenated derivatives thereof (i.e. —SOR⁶ or —SO₂R⁶ where R⁶ is alkyl), sulphonic acid and esters and amides thereof and substituted amides thereof (for example phenylsulphamyl, ethylsulphamyl, chloroethylsulphamyl) and a heterocyclic ring attached to the imidazopyridine system through a nitrogen atom, radicals, or a salt or N-oxide of said imidazopyridine, where such exist. Preferred compounds are those in which R⁵ is not —SR⁷.

Salts of the substituted imidazopyridines embraced by the present invention where R¹ is hydrogen may comprise ammonium salts, metal salts such as sodium, potassium, calcium, zinc, copper and magnesium salts, amine salts such as methylamine, ethylamine, dimethylamine, triethylamine, ethanolamine, triethanolamine and benzylamine salts. According to a preferred embodiment the salts are alkali metal salts. Generally the alkali metal salts are crystalline solids, readily soluble in water.

The salts may be prepared by reacting the imidazopyridine in aqueous or aqueous-organic solvent solution or suspension with an alkaline compound of the metal, such as the hydroxide, or with the amine, as appropriate, the metal salts may also be prepared by meta-thesis for example between the alkali metal salt of the imidazopyridine and a salt of the metal.

Other salts of the imidazopyridines which are embraced by the present invention are acid addition salts and quaternary ammonium salts.

The acid addition salts are formed between basic imidazopyridine and strong acids, for example hydrochloric acid, sulphonic acid and perchloric acid. The quaternary ammonium salts may be prepared by reacting the imidazopyridine with an alkylating agent, for example dimethyl sulphate, ethyl iodide and propylene dibromide.

According to a preferred embodiment of the invention, in the formula above Z¹ or Z² is a nitrogen atom.

Examples of the imidazopyridines according to the present invention which may be mentioned include:—

- 6-chloro-2-isopropylimidazo(4,5-b) pyridine,
- 6-chloro-2-tert.butylimidazo(4,5-b) pyridine and
- 6-chloro-2-ethylimidazo(4,5-b) pyridine.

The present invention is also for a biocidal composition and particularly a herbicidal composition which contains as an active component a substituted imidazopyridine as identified above. The biocidal composition also contains at least one material selected from carriers, wetting agents, inert diluents and solvents.

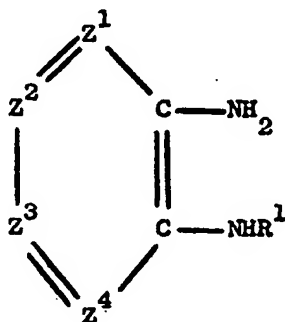
The present invention is also for the treatment of plants, the soil, land or aquatic areas, or materials, which comprises applying thereon or thereto a biocidal composition as identified above. The compounds and compositions according to the present invention are suitable for controlling detrimental organisms.

The substituted imidazopyridines according to the present invention generally possess biocidal activity. These compounds are useful mainly as herbicides, but they also find use as insecticides, molluscicides or fungicides.

The substituted imidazopyridines have been found to be of particular value as selective herbicides for pre-emergence use and are also useful for post-emergence use. With some crops, pre-emergence use is of greater importance. The compounds may also be used as total weedkillers.

The compounds of the invention, for example 6-chloro-2-isopropylimidazo-(4,5-b) pyridine, 6-chloro-2-tert.butylimidazo(4,5-b) pyridine and 6-chloro-2-ethylimidazo-(4,5-b) pyridine, are particularly useful as pre-emergent selective herbicides, for example for weed control in maize, soya beans, ground nuts and sugar cane.

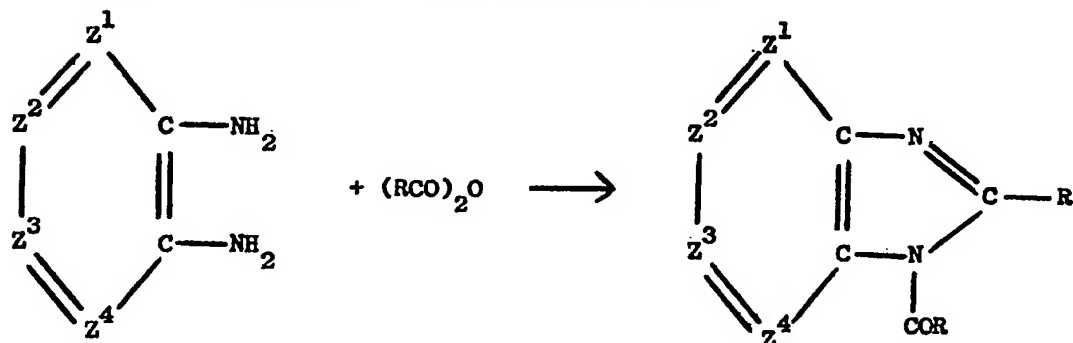
The substituted imidazopyridines according to the present invention may be prepared by reacting an ortho-diaminopyridine of the general formula:—



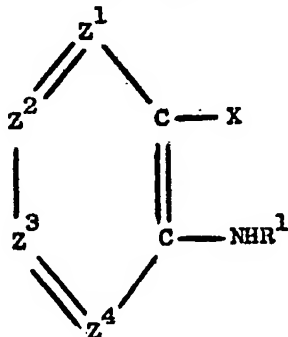
5 with an acid of the formula RCOOH or a functional derivative of the acid such as an acid halide, ester, amide or anhydride, where R, R¹, Z¹, Z², Z³ and Z⁴ have the significance indicated above. 5

10 Normally, where R is a lower alkyl group, the acid RCOOH is a liquid and the reaction is carried out by refluxing a solution of the corresponding diamino pyridine in an excess of the acid (suitably 10 to 15 times molar excess) for a period of 19—24 hours. In certain cases, longer heating gives increased yields. Where the acid RCOOH is a liquid of high boiling point or a solid, the reactants may be heated together in approximately equimolar proportions in the molten state for a shorter period of time. Solvents are not normally necessary but may be used if desired. 10

15 When an ortho-diaminopyridine unsubstituted on the nitrogen atoms is reacted with an excess of the anhydride of the acid RCOOH, the product is a 1(3)-acyl substituted imidazopyridine, according to the following formula:— 15



The substituted imidazopyridines according to the present invention may also be prepared by reacting an aminopyridine of the general formula:—

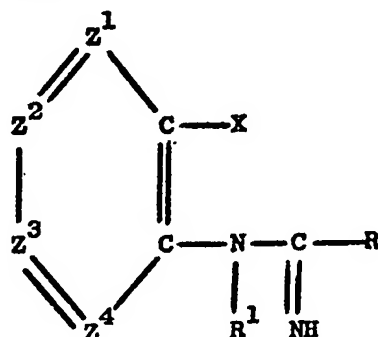


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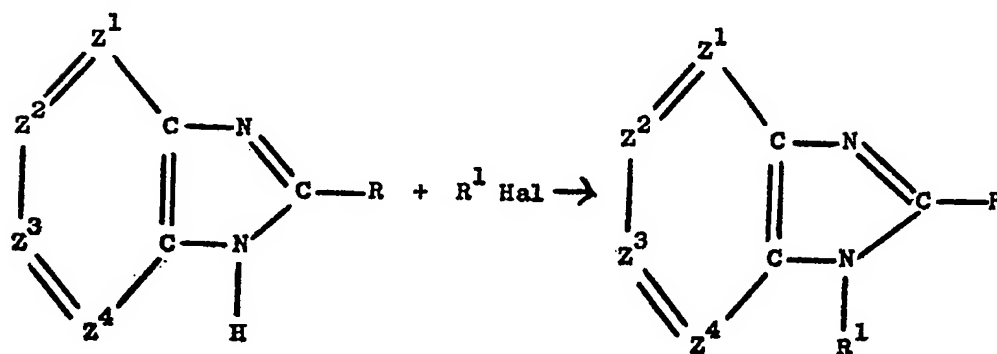
with a nitrile of the formula RCN, wherein X represents hydrogen or halogen and

R, R¹, Z¹, Z², Z³ and Z⁴ have the significance indicated above, to form the substituted amidine of the general formula:—



and cyclising this with a mild oxidising agent such as sodium hypochlorite to form the imidazopyridine.

The compounds where R¹ is not hydrogen can also be prepared by treating the corresponding compound where R¹ is hydrogen with a compound of the formula R¹-Hal, where Hal is a halogen, as indicated in the formula below:—



Many of the salts of the substituted imidazopyridines embraced by the invention are water-soluble, and these may be used in biocidal compositions, e.g. herbicidal compositions, as aqueous solutions with or without wetting or dispersing agents, organic solvents, stickers and the like, which are commonly incorporated in sprays for agricultural and related purposes. However, it is generally preferred to use the salts of the substituted imidazopyridines, possibly in association with a wetting agent.

If desired the substituted imidazopyridines or salts thereof may be dissolved in a water immiscible solvent, such as a high boiling hydrocarbon, suitably containing dissolved emulsifying agents so as to act as a self-emulsifiable oil on addition to water.

The substituted imidazopyridines or salts thereof may also be admixed with a wetting agent with or without an inert diluent to form a wettable powder which is soluble or dispersable in water, or may be mixed with the inert diluent to form a solid or powdery product.

Inert diluents with which the substituted imiazopyridines and salts thereof may be incorporated include solid inert media comprising powdered or divided solid materials, for example, clays, sands, talc, mica and fertilizers, such products either comprising dust or larger particle size materials.

The wetting agents used may comprise anionic compounds such as soaps, fatty sulphate esters such as dodecyl sodium sulphate, octadecyl sodium sulphate and cetyl sodium sulphate, fatty aromatic sulphonates such as alkyl-benzene sulphonates or butyl naphthalene sulphonate, more complex fatty sulphonates such as the amide condensation product of oleic acid and N-methyl taurine or the sodium sulphonate of dioctyl succinate.

The wetting agents may also comprise non-ionic wetting agents such as condensation products of fatty acids, fatty alcohols or fatty substituted phenols with

ethylene oxide, or fatty esters and ethers of sugars or polyhydric alcohols, or the products obtained from the latter by condensation with ethylene oxide, or the products known as block copolymers of ethylene oxide and propylene oxide. The wetting agents may also comprise cationic agents such as cetyl trimethylammonium bromide.

The biocidal compositions according to the present invention may contain in addition to the substituted imidazopyridines or salts thereof, other active materials such as herbicides, insecticides, fungicides and molluscicides. It has been found that particular advantages are obtained with mixtures with other herbicides.

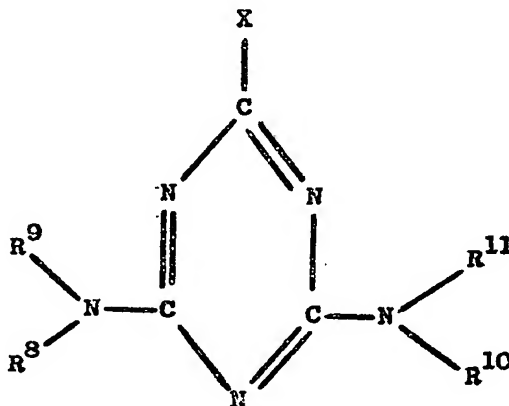
Accordingly, a further embodiment of the present invention is for a herbicidal composition which comprises a mixture of the substituted imidazopyridine as identified above and a second herbicide.

The second herbicide may be for example a phenoxyaliphatic acid, or a substituted urea or a triazine. In respect of the selective herbicidal compositions for post-emergence use, the second herbicide is suitably a substituted phenoxyaliphatic acid; in respect of selective herbicidal compositions for pre-emergence use, the second herbicide is suitably a substituted urea or triazine.

In such mixtures, the phenoxyaliphatic acid generally comprises one or more alkyl and/or halogen substituted phenoxyaliphatic acids, and their salts, for example alkali metal, amine and alkanolamine salts, and functional derivatives, for example esters and amides. These compounds may be of activity such that they are recognised as commercial herbicides, or may be of only slight herbicidal activity. Examples of the substituted phenoxyaliphatic acids which may be mentioned include 2,4-dichlorophenoxyacetic acid, 2-methyl-4-chlorophenoxyacetic acid; 2,4,5-trichlorophenoxyacetic acid, gamma-2,4-dichlorophenoxy-butyric acid, gamma-2-methyl-4-chlorophenoxy-butyric acid, alpha-2-methyl-4-chlorophenoxypropionic acid.

In such mixtures, the substituted urea generally comprises a tri- or tetra-substituted urea such as N'-parachlorophenyl-N,N'-dimethylurea, N-butyl-N'-(3,4-dichlorophenyl)-N-methylurea, N'-parachlorophenyl-O,N,N-trimethylisourea, N'-p-chlorophenyl-N-methoxy-N-methylurea, N,N-dimethyl-N'-phenylurea.

In such mixtures, the triazine herbicide generally comprises a compound of the general formula:—



where X is a halogen, OY group or SY group, where Y is an alkyl group, and R⁸, R⁹, R¹⁰ and R¹¹ are hydrogen or alkyl, such as 2-chloro-4,6-bisethylamino-1,3,5-triazine or 2-chloro-6-ethylamino-4-isopropylamino-1,3,5-triazine.

A further embodiment of the invention comprises a process for the control of weeds, which comprises the use of a mixture of a substituted imidazopyridine and a second herbicide.

The ratio of the substituted imidazopyridine to the second herbicide may vary over a wide range according to the particular compounds involved and the intended use. In general the ratio of substituted imidazopyridine to second herbicide lies in the range 1:0.1 to 1:15.

These mixtures are of particular value in the control of weeds, and may be more effective and economical than the components used alone. In some cases synergism is observed.

The following examples are given to illustrate the present invention. Parts and percentages are by weight unless otherwise indicated.

EXAMPLE 1

A solution of 2,3-diamino-5-chloropyridine (144 parts) in isobutyric acid (880 parts) was heated at reflux temperature for 24 hours. The excess acid was then removed by distillation under reduced pressure and the residual solid was recrystallised from toluene to yield 6-chloro-2-isopropylimidazo(4,5-b)-pyridine (137 parts, 70% yield) as light brown needles, melting point 190—192°C.

EXAMPLES 2—10

By analogous processes to that described in Example 1, starting from 2,3-diamino-5-chloropyridine and the appropriate carboxylic acid, the following substituted imidazo(4,5-b) pyridines were prepared:—

- 6-chloro-2-isopentylimidazo(4,5-b)-pyridine, melting point 208—210°C.,
- 6-chloro-2-isobutylimidazo(4,5-b)pyridine, melting points 207—208°C.,
- 6-chloro-2-(1'-ethylpropyl)imidazo(4,5-b)pyridine, melting point 183—184°C.,
- 6-chloro-2-cyclohexylimidazo(4,5-b)pyridine, melting point 238—240°C.,
- 6-chloro-2-methylimidazo(4,5-b)pyridine, melting point 276—277°C.,
- 6-chloro-2-ethylimidazo(4,5-b)pyridine, melting point 232—233°C.,
- 6-chloro-2-pentylimidazo(4,5-b)pyridine, melting point 194—196°C.,
- 6-chloro-2-propylimidazo(4,5-b)pyridine, melting point 217—219°C. and
- 6-chloro-2-*tert*-butylimidazo(4,5-b)pyridine, melting point 235—237°C.

EXAMPLE 11

A solution of 2,3-diamino-5-bromo-6-methylpyridine (202 parts) in isovaleric acid (1,020 parts) was heated at reflux temperature for 69 hours. The excess acid was then evaporated off under reduced pressure and the remaining solid recrystallised from a chloroform/petroleum ether mixture to give brown crystalline plates of 6-bromo-5-methyl-2-isobutylimidazo(4,5-b)pyridine, melting point 157—159°C.

EXAMPLE 12

A solution of 2,3-diaminopyridine (109 parts) in isobutyric acid (1,080 parts) was heated under reflux for 90 hours, then the solution was evaporated to dryness under reduced pressure.

Recrystallisation of the residue from benzene-light petroleum (b.p. 100—120°) furnished pale brown crystals of 2-isopropylimidazo(4,5-b)pyridine, m.p. 247—9°; in 70% yield.

Found on analysis: C, 67.20; H, 7.0
C₉H₁₁N₃ requires: C, 67.10; H, 6.85%

EXAMPLES 13—18

By an analogous process to that described in Example 1, the following compounds were prepared:—

- 2-Ethyl-6-nitroimidazo(4,5-b)pyridine, melting point 253—255°C.,
- 6-bromo-2,5-dimethylimidazo(4,5-b)pyridine, melting point 243—246°C.,
- 2-(1'-ethylpropyl)imidazo(4,5-b)pyridine, melting point 154—157°C.,
- 2-isobutylimidazo(4,5-b)pyridine, melting point 137—139°C.,
- 2-*tert*-butylimidazo(4,5-b)pyridine, melting point 249—251°C.,
- 2-*tert*-butyl-6-nitroimidazo(4,5-b)pyridine, melting point 233—235°C.

EXAMPLE 19

A solution of 2,3-diamino-5-chloropyridine (3.6 parts) in butyric anhydride (60 parts) was heated under reflux for 21 hours. The excess anhydride was distilled under reduced pressure, leaving an oil which solidified on cooling.

Recrystallisation of the product from light petroleum (b.p. 40—60°) (80 parts) furnished crystals, m.p. 92—4° (2.15 parts; 40%) of pure 1(3)-butyryl-6-chloro-2-propylimidazo(4,5-b)pyridine.

EXAMPLE 20

Using a method analogous to that of Example 19, replacing butyric anhydride by propionic anhydride, 1(3)-propionyl-6-chloro-2-ethylimidazo(4,5-b)pyridine, melting point 117—118°, was prepared.

EXAMPLE 21

5 A solution of phenyl chloroformate (1.45 parts) in dry acetone (16 parts) was added in one portion to a stirred suspension of the 2-isopropyl-5-methyl-6-chloroimidazo(4,5-b)pyridine (2.2 parts) in dry acetone (40 parts) containing triethylamine (1.2 parts). Following the addition, the mixture was heated under reflux (water-bath) for 1 hour. The reaction mixture was allowed to cool and the triethylamine hydrochloride was filtered; the filtrate was then evaporated to dryness under reduced pressure. 5

10 Recrystallisation of the residue from light petroleum (b.p. 80—100°) gave the crystalline product, m.p. 152—5°. Yield, 1.65 parts (48%) of 6-chloro-2-isopropyl-5-methyl-1(3)-phenoxy carbonylimidazo(4,5-b)pyridine. 10

EXAMPLE 22

15 Using a method analogous to that of Example 21, replacing 2-isopropyl-5-methyl-6-chloroimidazo(4,5-b)pyridine by 2-isopropyl-5-methyl-6-bromoimidazo(4,5-b)pyridine, 6-bromo-2-isopropyl-5-methyl-1(3)-phenoxy carbonylimidazo(4,5-b)pyridine, melting point 174—176°, was prepared. 15

EXAMPLE 23

20 12N Hydrochloric acid (0.6 ml.) was added to a solution of 2-*tert*-butyl-6-chloroimidazo(4,5-b)pyridine (1.04 parts) in absolute ethanol (12 parts); then, the solution was evaporated to dryness under reduced pressure. 20

Sublimation of the crude material at 180°/20mm. gave a white crystalline solid, m.p. 205—8° (1.12 parts; 91%) of 2-*tert*-butyl-6-chloroimidazo(4,5-b)pyridine hydrochloride.

EXAMPLE 24

25 In an analogous way to the processes of Examples 1—23 the following compounds were prepared: — 25

6-chloro-2-isopropylimidazo(4,5-b)pyridine,
6-cyano-2-allylimidazo(4,5-b)pyridine,
6-nitro-2-ethynylimidazo(4,5-b)pyridine,
30 6-amino-2-phenylimidazo(4,5-b)pyridine, 30
5-dimethylamino-2-benzylimidazo(4,5-b)pyridine,
5-morpholino-2-isopropyl(4,5-b)pyridine,
1(3)-benzyl-2-chloroethylimidazo(4,5-b)pyridine,
6-chloro-1(3)-para-nitrophenyl-2-*tert*-butylimidazo(4,5-b)pyridine,
35 6-chloro-1(3)-ethoxycarbonyl-2-methylimidazo(4,5-b)pyridine, 35
6-chloro-2-nitrophenylimidazo(4,5-b)pyridine,
6-chloro-2-chlorobenzylimidazo(4,5-b)pyridine,
6-bromo-2-methylcyclopropylimidazo(4,5-b)pyridine,
6-methyl-2-chloroethylimidazo(4,5-b)pyridine.

EXAMPLE 25

40 Finely ground 2,3-diamino-5-chloropyridine (287 parts) and lauric acid (400 parts) were mixed, and heated on an oil-bath maintained in the range 180—90° for 4 hours. The melt which solidified on cooling was dissolved in boiling benzene (3,000 parts). The oil which was deposited initially was rejected. On further standing, the decanted liquors furnished a crystalline solid, which gave cream crystals of 2-undecyl-6-chloromidazo(4,5-b)pyridine, m.p. 156—8°, after recrystallisation from benzene. Yield, 275 parts (45%). 45

On analysis, found: C, 66.05; H, 8.60

C₁₇H₂₆ClN₃ requires: C, 66.35; H, 8.50%

EXAMPLE 26

50 Seeds of peas, mustard, linseed, ryegrass, sugarbeet and oats were grown in John Innes potting compost in aluminium pans. When the plants were about 2 to 3 inches high and the first true leaves had expanded they were sprayed with aqueous acetone solutions of the imidazopyridine derivatives identified below at rates equivalent to 10 or 2½ pounds of active ingredient per acre. After seven days' growth in a controlled environment room the herbicidal activity of the compounds was assessed on a scale where 100 represents total kill and 0 represents no herbicidal effect. Results are tabulated below. 55

Compound	Rate lbs/acre	Herbicide Effect				
		Peas	Mustard	Linseed	Ryegrass	Sugarbeet
6-chloro-2-methyl- imidazo(4,5-b) pyridine	2½	0	80	40	15	35
6-chloro-2-ethyl- imidazo(4,5-b) pyridine	2½	5	90	85	35	85
6-chloro-2-isopropyl- imidazo(4,5-b) pyridine	10	15	100	100	70	100
2-isopropylimidazo- (4,5-b)pyridine	2½	20	70	30	0	20
6-chloro-2-pentyl- imidazo(4,5-b)pyridine	10	0	85	20	0	50

EXAMPLE 27

Seeds of peas, mustard, linseed, oats and ryegrass were sown in aluminium pans into John Innes potting compost which had been treated with imidazopyridine derivatives identified below at rates equivalent to 50 or 10 pounds per acre. After 22 days' growth in a controlled environment the herbicidal effect was assessed on a scale whereby 100 represents no development of the plants and 0 represents developments equal to that of plants grown in untreated soil. Results are tabulated below:

5

Compound	Rate lbs/acre	Herbicide Effect					
		Peas	Mustard	Linseed	Maize	Oats	Ryegrass
6-chloro-2-methylimidazo (4,5-b)pyridine	10	25	100	60	0	80	80
6-chloro-2-ethylimidazo (4,5-b)pyridine	10	50	100	100	50	100	100
6-chloro-2-isopropyl- imidazo(4,5-b)pyridine	50	50	100	100	65	90	100
6-chloro-2-pentylimidazo- (4,5-b)pyridine	50	25	100	100	60	95	100
2-isopropylimidazo(4,5-b) pyridine	10	25	100	100	0	80	85
1(3)-propionyl-2-ethyl-6- chloroimidazo(4,5-b)pyridine	10	60	100	99	50	90	100
6-chloro-2-propylimidazo- (4,5-b)pyridine	10	28	100	98	5	80	85
1(3)-butyl-2-propyl-6- chloroimidazo(4,5-b)pyridine	10	25	100	70	0	75	50
6-bromo-2-isobutyl-5-methyl- imidazo(4,5-b)pyridine	10	10	99	55	0	35	25
6-chloro-2-tert-butylimidazo- (4,5-b)pyridine	10	60	100	100	70	90	99

EXAMPLE 28

A wettable powder formulation was made up as follows:—

	2-Tert-butyl-6-chloroimidazo(4,5-b)pyridine	20 parts	
	The condensation product of lauryl alcohol with 5 mols of ethylene oxide	2 parts	5
5	Sulphonated naphthol/formaldehyde resin	7 parts	
	China clay	to 100	

EXAMPLE 29

An aqueous hydrochloride formulation was made up as follows:—

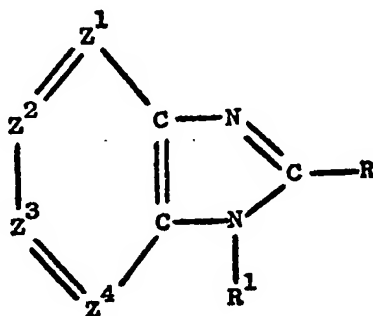
	6-Chloro-2-isopropylimidazo(4,5-b)pyridine	20 parts	10
10	Concentrated hydrochloric acid	3.7 parts	
	Industrial methylated spirits	20 parts	
	Water	to 100	

EXAMPLE 30

15 The wettable powder formulation of Example 28 was dispersed in water so as to apply $\frac{1}{2}$, 1, 2 and 4 pounds per acre (560 gm., 1.12 Kg., 2.24 Kg. and 4.48 Kg. per hectane) of 2-tert-butyl-6-chloroimidazo(4,5-b)pyridine in 20 gallons (90 litres) of spray liquid. The spray liquid was sprayed on fields containing potato and maize which had been sown the day before spraying. 7 Weeks after spraying the growth of the crops and the weeds were assessed and it was found there was no reduction in growth of the maize or potatoes at any rate of application compared with controls; there was 100% control of chickweed, fat hen, speedwell, matricaria and poppy at all rates of application, and 80% control of black bindweed at $\frac{1}{2}$ pound per acre (560 gm. per hectane) and 100% control at the other rates of application.

25 WHAT WE CLAIM IS:—

1) A biocidal composition which contains as an active ingredient a substituted imidazopyridine of the general formula:—



30 or a salt or N-oxide thereof, where R is a straight chain or branch chain alkyl, alkenyl, alkynyl, aryl, aralkyl, or cycloalkyl, substituted or unsubstituted; where R¹ is hydrogen, alkyl, aralkyl or aryl, substituted or unsubstituted, or —CY¹Y²R³ or —COR³, where Y¹ and Y² are oxygen or sulphur, and where R³ is alkyl or aryl, substituted or unsubstituted, or —SR⁴ where R⁴ is polyhalogenated alkyl, and where one of Z¹, Z², Z³ and Z⁴ is a nitrogen atom, and the remaining groups are CR², CR³ and CR⁴, where R², R³ and R⁴ are selected from hydrogen, alkyl, substituted alkyl, hydroxy, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, nitro, halogen, pseudo-halogen as hereinbefore defined, carboxy, carboxy ester, carboxy amide, N-mono-substituted or di-substituted carboxy amide, amino or mono- or di-substituted amino, thiol, alkylthiol, and oxygenated derivatives thereof as hereinbefore defined, sulphonic acid and esters and amides thereof, and substituted amides thereof and a heterocyclic ring attached to the imidazopyridine system through a nitrogen atom; and at least one material selected from the group consisting of carriers, wetting agents, inert diluents and organic solvents.

2) A biocidal composition as claimed in claim 1 where Z^1 or Z^4 is a nitrogen atom and the remaining groups of Z^1 , Z^2 , Z^3 and Z^4 are CR^2 , CR^3 and CR^4 as defined in claim 1.

3) A biocidal composition as claimed in claim 1 or claim 2 wherein the substituted imidazopyridine is selected from

6-chloro-2-isopropylimidazo(4,5-b)pyridine,
6-chloro-2-tert.butylimidazo(4,5-b)pyridine and
6-chloro-2-ethylimidazo(4,5-b)pyridine.

4) A biocidal composition as claimed in any of claims 1—3 which is a selective herbicidal composition.

5) Biocidal compositions substantially as hereinbefore described.

6) A herbicidal composition which comprises a mixture of a substituted imidazopyridine as identified in claim 1 and a second herbicide.

7) A herbicidal composition as claimed in claim 6 wherein the ratio of substituted imidazopyridine to second herbicide lies in the range of 1:0.1 to 1:15.

8) A herbicidal composition as claimed in claim 6 or claim 7 wherein the second herbicide is one or more of the compounds phenoxyaliphatic acids, substituted ureas and substituted triazines.

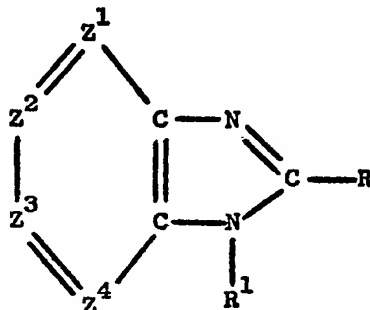
9) A herbicidal composition as claimed in any of claims 6—8 wherein the second herbicide is an alkyl and/or halogen substituted phenoxyaliphatic acid.

10) A herbicidal composition as claimed in claim 9 wherein the second herbicide is one or more of the compounds 2-methyl-4-chlorophenoxyacetic acid, 2,4-dichlorophenoxyacetic acid, 2,4,5-trichlorophenoxyacetic acid, gamma-2-methyl-4-chlorophenoxybutyric acid, gamma-2,4-dichlorophenoxybutyric acid, and alpha-2-methyl-4-chlorophenoxypropionic acid.

11) A herbicidal composition as claimed in any of claims 6—10 wherein the substituted imidazopyridine and the phenoxyaliphatic acid are used in the form of their salts.

12) A herbicidal composition as claimed in any of claims 6—8 wherein the second herbicide is one or more of the compounds N' -parachlorophenyl- N,N' -dimethylurea, N' -butyl- N' -(3,4-dichlorophenyl)- N -methylurea, N' -parachlorophenyl- O,N,N' -trimethylisourea, N' -p-chlorophenyl- N -methoxy-2-methylurea, N,N -dimethyl- N' -phenylurea, 2-chloro-4,6-bisethylamino-1,3,5-triazine and 2-chloro-6-ethylamino-4-isopropylamino-1,3,5-triazine.

13) A substituted imidazopyridine of the general formula:—



or a salt or N-oxide thereof, where R is a straight chain or branch chain alkyl, alkenyl, alkynyl, aryl, aralkyl, or cycloalkyl, substituted or unsubstituted; where R^1 is hydrogen, alkyl, aralkyl or aryl, substituted or unsubstituted, or $-CY^1Y^2R^3$ or $-COR^3$, where Y^1 and Y^2 are oxygen or sulphur, and where R^3 is alkyl or aryl, substituted or unsubstituted, or $-SR^7$, where R^7 is polyhalogenated alkyl, and where one of Z^1 , Z^2 , Z^3 and Z^4 is a nitrogen atom, and the remaining groups are CR^2 , CR^3 and CR^4 , where R^2 , R^3 and R^4 are selected from hydrogen, alkyl, substituted alkyl, hydroxy, alkoxy, substituted alkoxy, aryloxy, substituted aryloxy, nitro, halogen, pseudo-halogen as hereinbefore defined, carboxy, carboxy ester, carboxy amide, N-mono-substituted or di-substituted carboxy amide, amino or mono- or di-substituted amino, thiol, alkylthiol, and oxygenated derivatives thereof as hereinbefore defined, sulphonic acid and esters and amides thereof, substituted amides and a heterocyclic ring attached to the imidazopyridine system through a nitrogen atom.

14) A substituted imidazopyridine as claimed in claim 13 wherein Z^1 or Z^4 is a nitrogen atom and the remaining groups Z^1 , Z^2 , Z^3 and Z^4 are CR^2 , CR^3 and CR^4 as defined in claim 13.

16) A substituted imidazopyridine as claimed in claim 13 wherein R , R^1 , Z^1 , Z^2 , Z^3 and Z^4 are as defined in claim 13 but excluding the case where R^5 is $-SR^7$.

16) 6-chloro-2-isopropylimidazo(4,5-b)pyridine.

17) 6-chloro-2-tert.butylimidazo(4,5-b)pyridine.

18) 6-chloro-2-ethylimidazo(4,5-b)pyridine.

19) 6-chloro-2-methylimidazo(4,5-b)pyridine.

20) 6-chloro-2-pentylimidazo(4,5-b)pyridine.

21) 6-chloro-2-propylimidazo(4,5-b)pyridine.

22) 6-chloro-2-isopentylimidazo(4,5-b)pyridine.

23) 6-chloro-2-isobutylimidazo(4,5-b)pyridine.

24) 6-chloro-2-(1'-ethylpropyl)imidazo(4,5-b)pyridine.

25) 6-chloro-2-cyclohexylimidazo(4,5-b)pyridine.

26) 6-bromo-5-methyl-2-isopropylimidazo(4,5-b)pyridine.

27) 2-isopropylimidazo(4,5-b)pyridine.

28) 2-ethyl-6-nitroimidazo(4,5-b)pyridine.

29) 6-bromo-2,5-dimethylimidazo(4,5-b)pyridine.

30) 2-(1'-ethylpropyl)imidazo(4,5-b)pyridine.

31) 2-isobutylimidazo(4,5-b)pyridine.

32) 2-tert.butylimidazo(4,5-b)pyridine.

33) 2-tert.butyl-6-nitroimidazo(4,5-b)pyridine.

34) 1(3)-butyryl-6-chloro-2-propylimidazo(4,5-b)pyridine.

35) 1(3)-propionyl-6-chloro-2-ethylimidazo(4,5-b)pyridine.

36) 6-chloro-2-isopropyl-5-methyl-1(3)-phenoxycarbonylimidazo(4,5-b)pyridine.

37) 6-bromo-2-isopropyl-5-methyl-1(3)-phenoxycarbonylimidazo(4,5-b)pyridine.

38) 2-tert-butyl-6-chloroimidazo(4,5-b)pyridine hydrochloride.

39) Substituted imidazopyridines substantially as hereinbefore described.

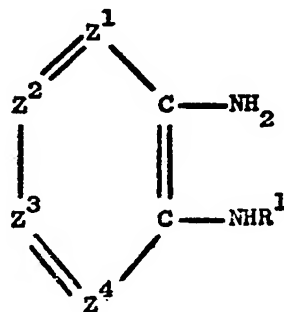
40) Substituted imidazopyridines substantially as hereinbefore described and illustrated in any of the preceding examples.

41) Ammonium, metal and amine salts of the substituted imidazopyridines as claimed in any of claims 13—40.

42) Acid addition salts of the substituted imidazopyridines as claimed in any of claims 13—40.

43) Quaternary ammonium salts of the substituted imidazopyridines as claimed in any of claims 13—40.

44) A process for the preparation of the substituted imidazopyridines as claimed in claim 13 which comprises reacting an ortho-diaminopyridine of the general formula:—



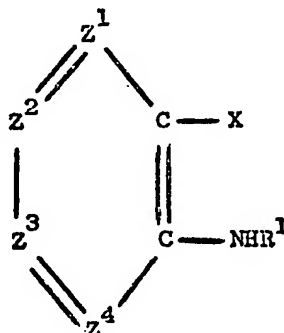
with an acid of the general formula $RCOOH$ or a functional derivative thereof, where R , R^1 , Z^1 , Z^2 , Z^3 and Z^4 have the significance indicated in claim 13.

45) A process as claimed in claim 44 wherein the functional derivative of the acid is the acid halide, ester, amide or anhydride.

46) A process as claimed in claim 44 or claim 45 wherein a solution of the diaminopyridine is refluxed with an excess of the acid.

47) A process as claimed in claim 44 or claim 45 wherein the diaminopyridine and the acid are fused together.

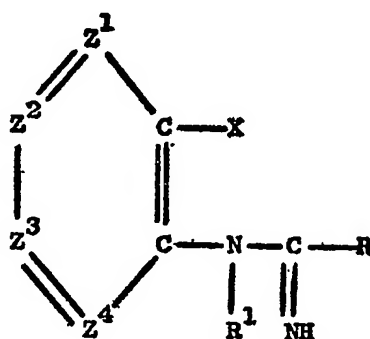
5 48) A process for the preparation of the substituted imidazopyridines as claimed in claim 13 which comprises reacting an aminopyridine of the general formula:— 5



with a nitrile of the formula RCN, wherein X represents hydrogen or halogen and R, R¹, Z¹, Z², Z³ and Z⁴ have the significance indicated in claim 13, to form the substituted amidine of the general formula:—

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and cyclising this with a mild oxidising agent to form the imidazopyridine.

49) A process for the preparation of the substituted imidazopyridines as claimed in claim 13 in which R¹ is a group other than hydrogen which comprises treating the corresponding compound where R¹ is hydrogen with a compound of the formula A—Hal where A is the said group other than hydrogen and Hal is a halogen.

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50) Processes for the preparation of substituted imidazopyridines substantially as hereinbefore described.

51) Processes for the preparation of substituted imidazopyridines substantially as hereinbefore described and illustrated in any of Examples 1—23.

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52) Substituted imidazopyridines when prepared by a process as claimed in any of claims 44—51.

53) A process for the treatment of plants, the soil, land or aquatic areas, or materials, which comprises applying thereon or thereto a substituted imidazopyridine as claimed in any of claims 13—40 or 52 or a composition as claimed in any of claims 1—12.

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54) A process for the treatment of plants, the soil, land or aquatic areas, or materials, substantially as hereinbefore described.

F. MURPHY,
Agent for the Applicants,
Chartered Patent Agent,
Fisons Limited,
Harvest House,
Felixstowe,
Suffolk.

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